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Strength, storage, and combustion characteristics of densified lignocellulosic biomass produced via torrefaction and hydrothermal carbonization

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HIGHLIGHTS

- Densification characterization of the raw and pretreated miscanthus is proposed.
- HTC pretreated miscanthus shows improved grindability and reduced ash yield.
- Energy density and O/C–H/C ratios of HTC-260 °C pellets are comparable to lignite.
- HTC pellets show improved hydrophobicity and resistance against water immersion.
- Torrefied pellets show low mass density and durability even compare to raw pellets.

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ABSTRACT

Lignocellulosic biomass has the potential to produce sustainable clean-green energy and other bio-based materials. However, due to the inferior physicochemical properties compared to coal, biomass is not regarded as an ideal feedstock for industrial applications. The work presented in this study evaluates the feasibility of two different thermal pre-treatments, torrefaction and hydrothermal carbonization (HTC), followed by densification. The densified and pretreated samples obtained from miscanthus feedstock were characterized in terms of the strength, storage, and combustion properties for energy applications. The results showed that both the thermal pre-treatments are promising methods for upgrading biomass. However, the HTC pellets showed considerably superior physicochemical properties when compared to the raw and torrefied pellets. The mass density (mass per unit volume) and volumetric energy density (HHV per unit volume) of the pellets produced via HTC at 260 °C was significantly higher (1036 kg/m^3, 26.9 GJ/m^3) compared to raw pellets (834 kg/m^3, 15.7 GJ/m^3) and torrefied pellets (820 kg/m^3, 16.7 GJ/m^3). Moreover, the HTC pellets showed improved hydrophobicity, reduction in ash content, reduction in alkali and alkaline earth metal content, and a considerable increase in the carbon content. Based on these results, the HTC pellets have potential for the heat and power applications, including replacing coal in the existing coal-fired power plants without any significant modifications.

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1. Introduction

Transformation towards developing a renewable and sustainable energy resource has gained tremendous attention due to the decline in the supply and environmental concerns associate with consumption of fossil fuels. Among all the renewable energy options, lignocellulosic biomass is the only carbon neutral energy resource that can be converted into any form of fuel including solid, liquid, or gas, which has made biomass an attractive fuel source for the energy production [1]. In addition to many other advantages, the use of biomass as a supplement to fossil fuel reduces the greenhouse gases (GHGs) and other harmful-toxic carcinogenic emissions. However, the lignocellulosic have poor structural heterogeneity, non-uniform physicochemical properties, low bulk density, low carbon content, high oxygen content, low energy density, high fibrous nature, high alkali and alkaline earth metal composition, high moisture content, and hydrophilic nature. These inferior properties results in highly inefficient transportation, handling, storage, combustion, and its conversion to bio-based

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materials for bioenergy development [2]. In order to address the these limitations, lignocellulosic biomass has to be pre-processed or pre-treated before it is utilized as an efficient energy resource [3].

Compaction or densification of biomass into a regular shape product(s) like pellets, briquettes, and cubes is one way to increase the bulk density and overcome handling difficulties. Pelletizing, the densification of biomass into pellets, has obtained a great deal of worldwide interest in recent years as an efficient technique in improving the logistics of biomass. Densification of agricultural (straw and grasses) and woody (chips) biomass into pellets can increase the bulk density from 40–200 to 600–800 kg/m^3 [4]. Thus, the densification of biomass can significantly reduce the overall transportation and handling costs associated with biomass processing. However, owing to the hydrophilic nature of biomass, pellets produced from raw biomass tends to shatter when they come in contact with water or relatively high humidity conditions. The presence of high moisture content in biomass feedstock/pellets can also influence fungal growth, which can cause the material to decompose during storage.

The chemical reactions (generally oxidation) or anaerobic microorganism activity in biomass feedstock/pellets can produce heat at a sufficient rate that it can cause self-heating of the biomass stockpile. This can lead to self-ignition or other harmful toxic gaseous emissions [5]. Therefore, the pellets produced from raw biomass are not meant for long term storage (either indoor or outdoor) without the use of environmentally controlled storage structures. The construction of these structures can increase the overall storage cost associated with biomass feedstock or pellets.

Densification in combination with the thermal pre-treatments like torrefaction is often proposed as an alternate to improve the physicochemical properties of biomass [6,7]. During torrefaction, biomass is heated in an inert atmosphere at temperatures of about 200–300 °C for residence times of 30 min to a couple of hours. This process results in approximately 30% mass loss, with only 10% of the energy contained within the biomass lost in the form of gases. Therefore the specific energy density of the torrefied solid product is increased [7]. As such, the pellets produced from torrefied biomass are more cost competitive than the regular “white pellets” (raw pellets) as they have an increased bulk energy density (i.e. energy per unit volume).

Other advantages associated with the torrefaction process include reduced moisture content, improved resistance to water damage and microbial growth, and increased friability which makes torrefied pellets easier to grind [8]. While torrefied pellets represent a significant improvement over the conventional white pellets, these pellets present handling issues due to their weak strength and low durability. This can cause them to break apart easily and generate dust, which causes a risk of explosion. The bulk energy density and grindability of the torrefied pellets are not comparable to that of coal and more importantly the high inorganic metallic content in ash still remains a significant challenge for biomass combustion [9,10]. As the torrefaction process is unable to remove the alkali and alkaline earth metals from biomass ash, the use of torrefied biomass in conventional pulverized coal boiler systems is highly inefficient [11]. A research has demonstrated that torrefied biomass was only able to replace 50% of the coal used in a coal fired boiler. This was due to the lower heating value (HHV) of biomass, fouling issues and low grindability compared to coal [12].

Addition of binding agents can improve the durability of torrefied pellets. However the addition of such binders may increase the overall manufacturing cost of the pellets and may also negatively impact the combustion behavior. Pre-drying the feedstock may be required before torrefaction because the energy input and quality of end product significantly depend on the moisture content of the feedstock. The drying methods for biomass are highly energy consuming processes that require a significant financial load in the torrefaction and pelletization process, which makes the torrefaction of wet biomass like food waste impractical [13,14]. In order to improve the densification characterization of biomass without the expense of binders or adhesives, there is a need to develop an effective technique to produce pellets that have potential to replace coal at thermal power plants without any modification to the system.

A relatively new approach of hydrothermal carbonization (HTC), also referred to wet torrefaction, could potentially address these limitations of biomass. HTC is performed at the temperature range of 180–260 °C during which biomass is submerged in water and is heated in a confined system under pressure (2–6 MPa) for 5–240 min [15]. As the process itself is carried out in the presence of water it thus eliminates the pre-drying requirement of feedstock. The HTC process results in the formation of three different products: solid (hydrochar), liquid (aqueous soluble) and gaseous (mainly CO_2) products. The properties and percentage distribution of the final products strongly depends upon the process conditions [16]. Although both reaction time and temperature have been observed to influence the physicochemical characteristics of products, the reaction temperature remains the governing process parameter [17]. Hydrochar is the desired product in the HTC process, which exhibits unique and superior physicochemical properties compared to biochar (from pyrolysis and torrefaction), along with several value-added industrial applications [18].

Hydrochar is highly hydrophobic and friable, and also has the increased percentage of lignin and aqueous soluble materials compared to raw biomass. It is expected that using hydrochar for densification purposes can improve the pelletability of the biomass [19]. Secondly, since the process is carried out in the presence of liquid water, it can demineralize the elemental inorganic composition by precipitating the minerals in the liquid by-product stream. Reduction of the alkali and alkaline earth metal content from biomass would potentially mitigate the challenges such as slagging, scaling, and fouling in boilers during biomass combustion. The lack of energy intensive drying processes, high conversion efficiency, and a relatively low operating temperature and residence time range are significant advantages offered in the HTC process compared to other conventional thermal pre-treatments like torrefaction [20].

Previous research has primarily focused on woody biomass in developing sustainable energy production. However, purpose grown energy crops like miscanthus also represents a significant share in the bioenergy development, as these crops grow quickly and require less maintenance [21]. An extensive variety of literature is available on torrefaction and densification of woody and agricultural biomass. However, no study exists that has examined the comparative assessment of such crops for producing high energy dense products via HTC and torrefaction pre-treatments. The primary goal of the work presented in this study is to compare the physicochemical properties and densification characterization of raw, torrefied, and HTC pretreated miscanthus feedstock in terms of the energy density, hydrophobicity, compression strength, and durability.

2. Materials and methods

2.1. Materials

To compare and evaluate the densification performance of HTC and torrefied biomass, miscanthus (*Miscanthus × giganteus*, ‘*Nagara*’) feedstock was considered in this study. The feedstock was harvested in May 2013 and collected from a privately owned farm in Drumbo, Ontario. Prior to the HTC and torrefaction experiments, the feedstock was manually chopped into samples of lengths ranging from 20 to 25 mm to prepare a more uniform sample. These prepared samples were then stored in a sealed plastic bag until treatment.

2.2. Experimental setup

2.2.1. Hydrothermal carbonization

HTC of biomass was carried out using Parr 600 ml bench top reactor (Moline, IL) fitted with the glass liner (762HC3) as shown in Fig. 1. To analyze the effect of different operating conditions on biomass, the experiments were performed at different reaction temperatures (190, 225, 260 °C), residence times (5, 15, 30 min) and feedstock-to-water ratios or solid load (1:6 & 1:12 (w/w)). The temperature of the system was controlled using a Proportional-Integral-Derivative (PID) temperature controller. The reactor pressure was not controlled in the experiments and was kept autogenic with the vapor pressure of water at the corresponding reaction temperature. The pressure inside the reactor ranged from 1 to 5 MPa during the experiments, as indicated by the pressure gauge attached to the reactor.

Prior to the reaction, 10 g of miscanthus feedstock was mixed with the deionized water in the different ratios and was manually stirred for 2–3 min to ensure complete wetting. The reactor was heated up to the required temperature in approximately 20–30 min and was then maintained at the reaction temperature for the desired time period. It should be noted that the pre-heating time for the reactor would also play an important role in the HTC reaction chemistry because a higher reaction temperature would require a longer pre-heating time. However, in this study for the data analysis purpose, the reaction temperature was defined as the isothermal holding time period (i.e. 5 min at 190, 225, and 260 °C). The temperature and pressure profiles in the reactor during HTC experiments are shown in Fig. 2. Later, to further quench the reactions, the reactor was immersed in cold water and was cooled down to room temperature in about 5–7 min. Once the inside temperature of the reactor dropped to room temperature, the pressure release valve was opened under the fume hood and the gaseous products were allowed to escape. The solid and liquid products were separated using filter paper (20 μm) and were collected for further analysis (data not shown here for liquid analysis). The hydrochar samples were dried overnight at 103 °C before analysis. The experiments were repeated three times to ensure the reproducibility and consistency.

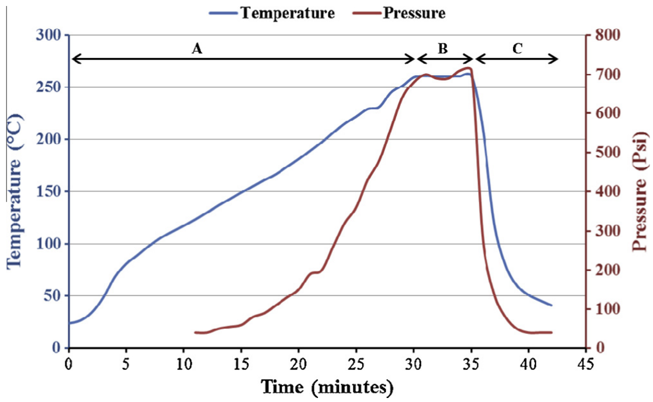

Fig. 2. Temperature and pressure profile for HTC experiment. Zone A: reactor heat-up time, zone B: reaction time, zone C: cooling time.

2.2.2. Dry torrefaction

Torrefaction experiments were performed using a macro thermo-gravimetric analyzer (TGA) (see Fig. 3) that was designed and fabricated in the machine shop at University of Guelph [22]. The reactor consist a stainless steel tube heated by four electric heaters of 1.25 KW capacity kept in close contact with the reactor wall. A small perforated basket made of stainless steel fitted with a ceramic crucible and attached to the balance to hold sample. For the each test, approximately 5 g of miscanthus was placed inside the crucible. The reactor was then heated to 260 °C with the heating rate of 10 °C/min and was maintained for 30 min. During torrefaction experiment, to prevent combustion, the reactor was continuously purged with the nitrogen gas (10 ml/min) to maintain an inert atmosphere inside the reactor. The nitrogen gas passed through a pre-heater (temperature controlled) before purging inside the reactor. After the desired reaction period, the sample was cooled down to room temperature while maintaining the continuous flow of nitrogen through the reactor. The remaining solid sample was collected and placed inside a sealed bag plastic until analysis. The torrefaction experiments were repeated three times to ensure the reproducibility and consistency.

2.2.3. Densification

The densification experiments were performed using a similar method used by a previous study on the pelletization of loblolly

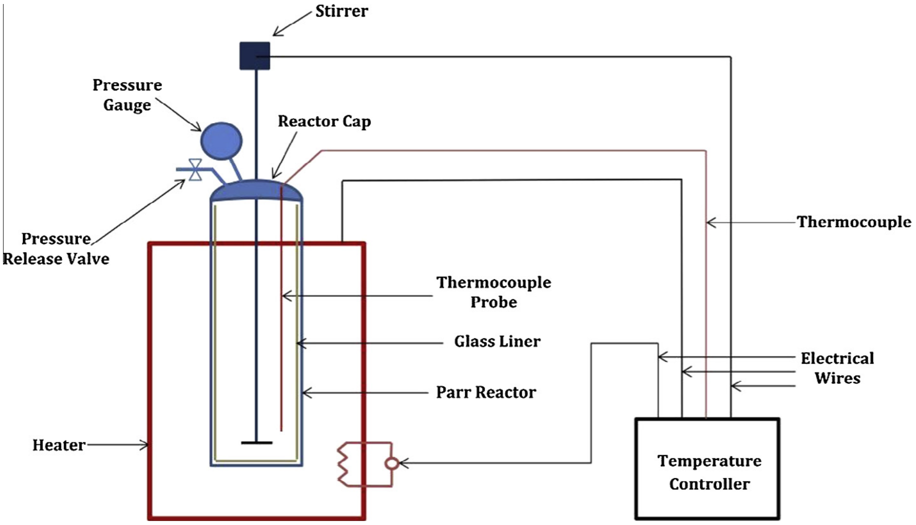

Fig. 1. HTC experimental setup.

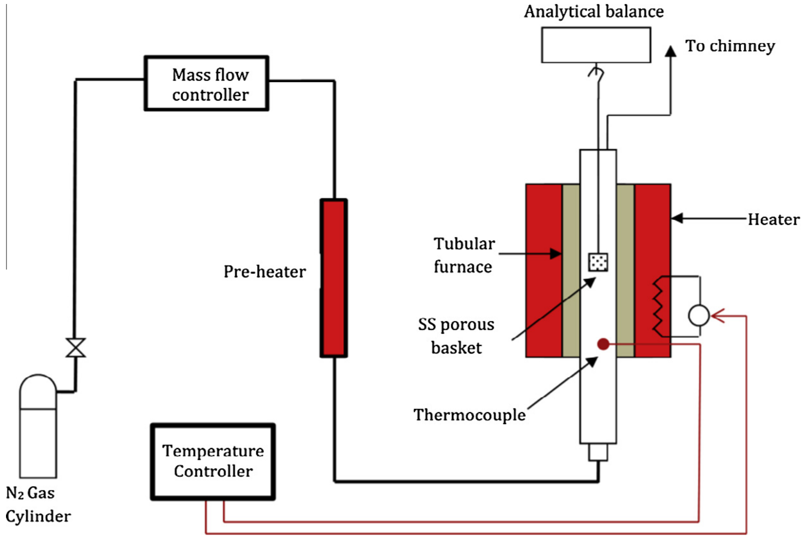

Fig. 3. Torrefaction experimental setup.

pine [20]. Initial moisture content and particle size distribution of a feedstock plays an important role in the pelletization process. Both raw and pretreated miscanthus samples were milled using a planetary ball mill grinder (Retsch PM-100). The milled samples were then sieved to the particle size range of less than 710 µm. The moisture in the feedstock during pelletization acts as a binder and lubricant [23]. Both the raw and pre-treated miscanthus samples were exposed to the standard room conditions for at least 24 h prior to pelletization, in order to bring them to the equilibrium moisture content (EMC). The EMC of the raw, HTC-190, HTC-225, HTC-260, and torrefied-260 samples were 10.95%, 7.54%, 6.22%, 3.52%, and 6.32%, respectively.

Pelletization of the samples was performed using a Parr single-pellet press (model#2912) modified in the machine shop at the University of Guelph. The pellet press consists a cylindrical die (1/4 in. in the diameter) made of hardened stainless steel, with a load cell and a band heater attached to it. The temperature of the die attached to the heater, was controlled using a PID temperature controller and set to 100 °C. The bottom of the die was closed using a removable backstop plate. After the temperature reached equilibrium, approximately 0.5 g of the sample was manually placed inside the die and compressed to a pressure of 8.6 MPa, using a lever attached to the pellet press (Fig. 4(A) and (B)). The sample was held under pressure for 30 s and released. After the compression, the backstop plate was removed from the die and the pellet was pressed out of the die channel using the same piston that was used for compression (Fig. 4(C)). The pellet samples were left undisturbed for 1–2 min and were then kept in sealed plastic bags for further analysis. To ensure the reproducibility and consistency, the densification, experiments were repeated three times.

2.3. Analytical methods

2.3.1. Proximate and ultimate analysis

The proximate analysis (ash, volatile matter and fixed carbon) of solid samples was carried out according to the ASTM standards. The measured amount of sample was placed in the muffle furnace (Thermo Scientific-F48055-60) maintained at 103 ± 2 °C for at least 16 h and then moved to a desiccator, containing silica gel, for cooling. The samples were then re-weighed and the change in the initial and final weight was expressed as percentage moisture (ASTM-E871). The dried solid samples were then ignited at 575 °C for 5 h in a muffle furnace to determine percentage ash (ASTM-E1755). The volatile matter of solid samples was measured by firing at

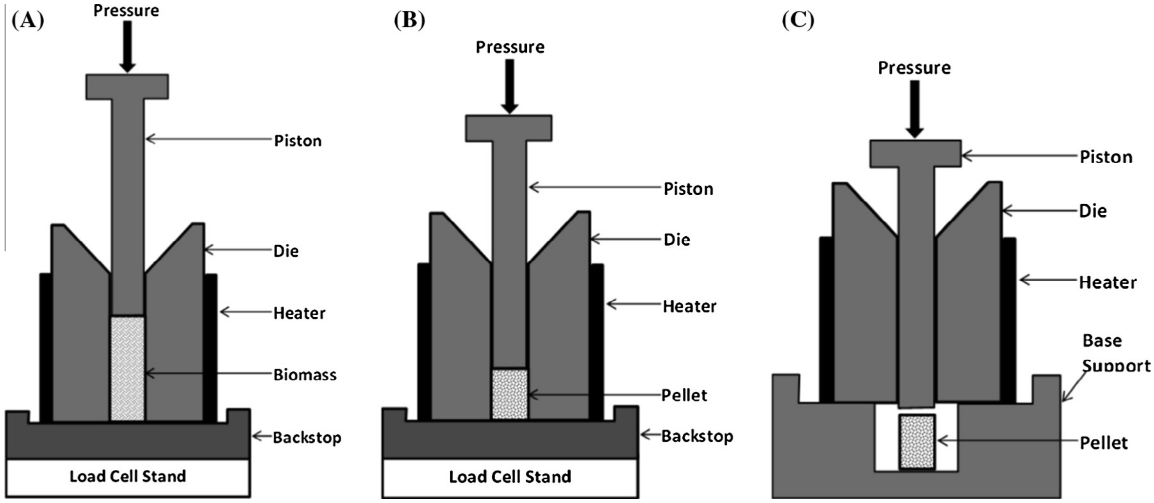

Fig. 4. (A) Pelletization setup, (B) pellet formation and (C) pellet extrusion.

950 °C for 7 min (ASTM-E872). The ash, moisture and volatile matter contents were subtracted from 100% to determine the fixed carbon content of the samples. The ultimate analysis (carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O)) of solid samples was measured using elemental analyzer (Thermo Fisher Flash EA-1112).

2.3.2. Higher heating value

The higher heating values (HHV) of raw and pre-treated solid samples were determined using IKA bomb calorimeter (C-200). All the samples were oven dried at 105 °C for 24 h prior to analysis.

2.3.3. Mass and energy density

The mass density of the pellets was expressed as the ratio of the mass to volume and a stereometric method was used to calculate the density of each pellet. The method is based on the measurement of dimensions (e.g., diameter and length) of a regular shape product. Each single pellet sample was weighed to the nearest value of 0.0001 g using an analytical balance (Mettler Toledo-MS204S). The volume of the each pellet sample was determined by measuring the volume of the pellet (cylinder in this case) using a digital caliper (Mastercraft, 58-6800-4). The volumetric energy density was calculated by multiplying the mass density of the pellet with the HHV of the pellet.

2.3.4. Compression strength

The compression strength of the pellets was measured using an Instron machine (model#5965). The method was adopted from a previous study [24]. Each single pellet was placed between two horizontal plates and compressed at a rate of 25 mm/min (Fig. 5). A data logger connected to the machine recorded the force (F) applied on the pellet. The maximum force a pellet could withstand, before the fracture or rupture of a pellet, was measured as the value for the compression strength.

2.3.5. Durability

The forces acting on pellets during unloading process from trucks on to the ground or during feeding from the chutes into bins at pellet manufacturing plants can be simulated by measuring the impact resistance, the drop resistance or the shattering resistance test. A drop resistance method was used in this study to determine the durability of the raw and pretreated miscanthus pellets [4]. Each pellet sample was dropped from 1.85 m height on a metal plate 4 times. The change in the weight percentage after the dropping test was expressed as the pellet durability.

2.3.6. Hydrophobicity

2.3.6.1. Equilibrium moisture content. The thermal pre-treatments are often proposed to improve the storage behavior or hydrophobicity of biomass. To confirm the validation of the above statement, the pellets were tested for the equilibrium moisture content (EMC). EMC is defined as the moisture content of the sample in thermodynamic equilibrium with the moisture in the surrounding atmosphere, at a given relative humidity, temperature, and pressure. To determine the EMC of raw and pre-treated miscanthus pellets, the samples were exposed to a controlled environment (relative humidity: 48–52% at 22–23 °C) for 24 h. After exposure samples were dried in an oven at 103 °C for 16hours. The change in the weight before and after drying was expressed as the percentage moisture adsorbed or EMC.

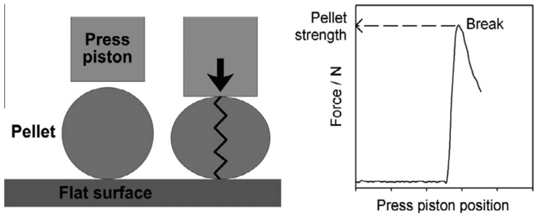

Fig. 5. Radial compression of pellets to test the compression strength [24] (adapted with permission from publisher).

2.3.6.2. Water resistance. Pimchuai and his co-authors [6] demonstrated the water resistance capacity of raw and torrefied biomass by immersing the samples in the water for 2 h. The samples were then allowed to dry in room conditions and the change in weight was expressed as the percentage moisture absorption. Using the same method, both raw and pre-treated pellets were immersed in the water for 2 h. Later the pellets were removed and the excess water was drained by placing the pellets on an adsorbent paper. The pellets were then gently placed on an aluminum sheet and were exposed to a controlled environment (relative humidity: 48–52% at 22–23 °C) for 4 h. The final material was then weighed and the change in the weight was expressed as the moisture content.

3. Results and discussions

3.1. Proximate and ultimate analysis

Both the proximate and ultimate analysis of raw, hydrochar, and torrefied miscanthus samples are summarized in Table 1. Proximate analysis is the most common method used to determine the quality of coal and other solid fuels. Biomasses generally have high volatile matter content and therefore show poor combustion efficiency and high harmful emissions when directly combusted [25]. Moreover, the co-firing of biomass with coal is highly problematic due to the difference in the bulk and energy density, volatile matter content, and combustion temperature [25]. The results show that the fraction of volatile matter decreases and percentage fixed carbon increases with an increase in the HTC reaction temperature.

Hydrochars produced at low temperature (190 and 225 °C) show similar behavior to that of the raw biomass. Similar performance was also observed for the torrefied miscanthus, even for significantly high reaction conditions (260 °C for 30 min). However, the hydrochar samples produced at high temperature (260 °C) show considerable reductions in the volatile matter and increases in the percentage fixed carbon. High inorganic elemental composition in biomass ash causes challenging issues like fouling and slagging in boilers which significantly can affect the thermal efficiency of a system and can lead to the corrosion of boiler tubes. Ash yield is defined as the ratio of percentage ash in the hydrochar to the percentage ash in the raw biomass multiplied by the mass yield at the corresponding pre-treatment temperature [26]. For the hydrochar samples significant reduction in ash yield was observed with an increase in reaction temperature. The reduction in the ash yield is directly related to the removal of the inorganic elemental composition (reduction by 20–70%) from hydrochar into the liquid by-product stream [17]. Table 2 shows the effect of the HTC and torrefaction process on the inorganic yield of hydrochar and torrefied biomass. Inorganic yield is expressed as the ratio of inorganic mass content in the pretreated miscanthus to the inorganic mass content in the raw miscanthus multiplied by the mass yield at a corresponding reaction temperature. It can be observed that the HTC process is able to remove 30–80% of the inorganic content from raw biomass. The removal capacity of the inorganic elements (except for the phosphorous) was also demonstrated to increase with an increase in the HTC reaction temperature [17]. The unexpected trend observed for phosphorous might be due to its

Table 1
Proximate and ultimate analysis of raw and pre-treated miscanthus.

Material	Operating conditions		Mass yield	Ultimate analysis					Proximate analysis		
Miscanthus	Temperature (°C)	Time (min)	Wt. (%)	C (%)	H (%)	N (%)	S (%)	O (%)	VM (%)	FC (%)	Ash (%)
Raw	–	–	–	46.7	6.0	0.2	0.0	45.3	87.5	11.7	0.8
HTC	190	5	83.5	48.8	6.0	0.2	0.0	44.7	83.8	15.7	0.5
HTC	225	5	66.9	49.6	6.0	0.3	0.0	41.8	81.9	17.5	0.7
HTC	260	5	47.8	61.2	5.3	0.4	0.0	31.6	68.9	30.3	0.8
Torrefaction	260	30	84.9	49.6	5.7	0.1	0.0	42.2	84.8	14.2	0.9

Table 2
Effect of pre-treatment on alkali and alkaline metal yield in solid product.

Metal	Inorganic yield (%)				
	Raw	HTC-190 °C	HTC-225 °C	HTC-260 °C	Torrefied-260 °C
Calcium	100.00	69.06	54.94	52.02	85.07
Magnesium	100.00	46.04	37.52	37.83	75.62
Phosphorous	100.00	21.92	27.92	39.41	50.80
Potassium	100.00	25.08	22.71	19.24	71.37
Sodium	100.00	66.40	48.96	36.38	89.24
Sulfur	100.00	64.59	57.43	54.05	54.01
Iron	100.00	27.99	25.66	27.17	82.27

non-metallic properties. Among all the inorganic elements analyzed in this study, only phosphorous and sulfur were non-metals. However, phosphorous and sulfur did not show similar behavior during HTC of miscanthus. Different inorganic elements in a biomass feedstock may show completely different catalytic properties and reaction mechanisms during the HTC process. However, the effect of the different inorganic elements in biomass on the HTC reaction chemistry is presently unknown. Hence, further in-depth research on the reaction behavior of different inorganic elements (both metals and non-metals) under varying HTC operating conditions may reveal the hidden secrets, which could be highly beneficial to the agro-chemical industries. These observations are consistent with the findings reported in the literature [26], and suggest that biomass pretreated with HTC at high temperatures can be co-fired with coal in the existing boiler systems without any significant modifications.

The ultimate analysis of both raw and pre-treated miscanthus samples is shown in Table 1. As expected, the percentage of carbon increases, while the percentage of oxygen decreases with an increase in HTC reaction temperature. The ultimate analysis of miscanthus torrefied at 260 °C does not show considerable improvements in carbon content. Similar results were observed for the hydrochar samples produced at low temperature (190 and 225 °C). It was also found that for the hydrochar samples obtained from HTC (190, 225 °C) and torrefaction (260 °C) the percentage of carbon remained almost the same; however the mass yield showed an inconsistent trend. The effect of different thermal pre-treatments of lignocellulosic biomass on the mass yield, HHV, and energy yield are discussed earlier [17]. The difference in the mass loss of the same feedstock in the two different thermal pre-treatments is mainly due to the variation in the degradation of biomass polymers. The extent of degradation of biomass polymers significantly depends upon the reaction medium in which the process is carried out [15]. Under hydrothermal conditions, the presence of subcritical water causes biomass polymers (mainly hemicellulose) to partially transform into an aqueous phase and therefore cause a significant mass loss of the solid product.

Decarboxylation, dehydration, de-carbonylation, de-methoxylation, intermolecular derangement, condensation, and aromatization are some of the proposed chemical reactions that take place during the thermal pre-treatment of biomass [27]. However, in the HTC process the reaction mechanism is initiated by hydrolysis, due to the presence of the hot compressed water. This results in cleavage of ether and ester bonds between monomeric sugars through the addition of one molecule of water [28], which thereby reducing the activation energy levels of biomass polymers [15]. Hence, the degradation of hemicellulose and the mass loss of solids in the HTC process are relatively higher compared to the torrefaction process.

During the analysis of HTC liquid by-product [29], the presence of intermediate oxygenated compounds and total organic carbon was observed. This explains the transformation of carbon and oxygen based compounds from the biomass into the aqueous phase, which causes the significant mass loss of hydrochar. The CHNSO analysis on a mass fraction basis, determined that the equivalent removal percentage of the CHNSO elements from hydrochar samples might have been responsible for the consistent trend observed for solid samples (190, 225 °C) during CHNSO analysis. However, with further increase in reaction severity (i.e. the reaction temperature at 260 °C), the high quality intermediate compounds like 2,5-HMF (Hydroxy-methyl-furfural) are formed that have high HHV. The precipitation of such compounds in the porous structure of hydrochar would increase the overall HHV (carbon content) of hydrochar. This phenomenon explains the reason behind the high carbon content and low oxygen content observed for hydrochar samples produced at 260 °C.

To analyze the variation in elemental compositions, the atomic ratios of hydrogen to carbon (H/C) and oxygen to carbon (O/C) of both raw and pre-treated samples were displayed in Fig. 6 (Van-Krevelen diagram [10]). The "Van Krevelen diagram" provides the general information about atomic ratios (O/C–H/C) of typical fuels, such as biomass, peat, and different types of coals. For comparison, the atomic ratios for the polymeric composition of lignocellulosic biomass were plotted on the diagram [30]. A fuel with the low O/C–H/C atomic ratio is considered highly favorable because of the decreased smoke, water vapor and energy losses experienced during combustion [31].

It is clear from the Van-Krevelen diagram that raw biomass has low a carbon content and high oxygen content compared to coal. Due to the removal of water and carbon dioxide, pretreated biomass contains low O/C–H/C atomic ratios when compared to raw biomass and therefore is more a coal-like product. However, depending upon the degree of pre-treatment (i.e. the process operating conditions) the physicochemical properties of a fuel can be

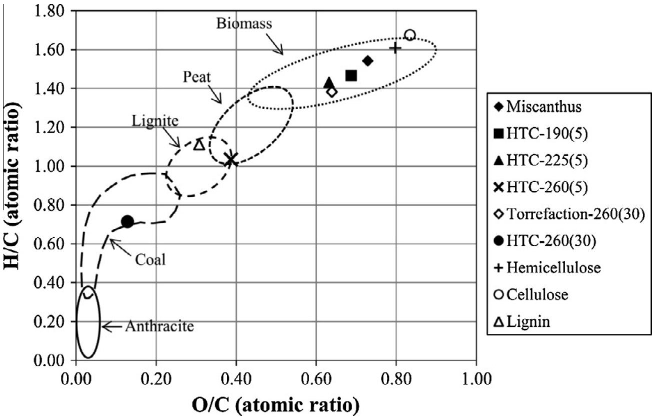

Fig. 6. Atomic H/C–O/C ratios of raw and pretreated miscanthus.

far different from coal. Like in case of torrefied (at 260 °C) and HTC (at 190 °C and 225 °C) miscanthus, the O/C–H/C ratios of the fuel were slightly reduced but are still similar to that of raw biomass, whereas for the hydrochar samples produced at 260 °C contained atomic ratios close to that of lignite.

In an HTC experiment (data not shown) at very severe operating conditions, i.e. highest reaction temperature (260 °C) and highest residence time (30 min), the combustion properties of the hydrochar were surprisingly improved and its position on the Van Krevelen diagram was found in the range of coal. This shows that the effect of reaction time on the extent of carbonization of hydrochar samples is highly prominent for high reaction temperatures. In contradiction to the expected low carbonization with an increase in the residence time at high reaction temperatures, a longer residence time would increase the process severity and therefore, significantly affect the overall energy density (or carbon percentage) of hydrochar samples. This phenomenon is due to the continuous polymerization of aqueous soluble products in the aqueous phase, which might later precipitate into the porous structure of insoluble hydrochar [27]. The samples were also analyzed for the characterization of organic acids and furfurals; the results for the formation of intermediate compounds and structural surface of hydrochar samples are reported in another study [29]. The main reason behind the strong carbonization in HTC is due to the presence of water as a reacting medium. This results in the reaction mechanism being initiated by hydrolysis, which exhibits lower activation energy levels than other conventional thermal pre-treatment decomposition reactions [15].

3.2. Mass and nergy density

Mass and energy density of pellets are the two parameters that are important in the transportation and handling economics of the wood pellets. Low bulk density of raw biomass results in inefficient logistics and challenges for the biomass processing industries [4]. Low carbon content and high oxygen content of raw biomass further reduces the HHV and overall bulk energy density [32]. A fuel with high bulk density and high energy density will be less expensive to transport and store, as it occupies less space to be stored or transported per unit of energy.

Table 3 shows the effect of densification on the mass density, HHV, and energy density of raw and pretreated miscanthus samples. The mass density of an oven dried miscanthus sample was observed around 321.09 ± 10 kg/m^3, which is much higher when compared to the values reported in the literature for miscanthus [33]. Generally for woody and agricultural biomass, bulk density is the more appropriate term/method, when referring to the density of a biomass at the industrial scale. While calculating the bulk density of a biomass, the volume of voids is also included in the measurement, however, in this study the mass density was calculated for the each single pellet by assuming it was a cylinder. The mass density is always higher than the bulk density of a biomass feedstock due to the elimination of volume occupied by voids. In this study the mass density of raw miscanthus increased by about 260% after compression.

The HHV of the raw biomass was measured both before and after densification. As no compositional change should take place in biomass at low temperature densification (100 °C) because other than extractives in the biomass, most of the polymeric (hemicellulose, cellulose, and lignin) composition of biomass does not start reacting until the material temperature reaches 180 °C [20,34], thus except for the extractives in the biomass no compositional change should take place at low temperature densification (100 °C). Also no external binding material was used for the densification of raw and pre-treated biomass, therefore, as expected, the HHV of the raw and pretreated biomass remained relatively unaffected after densification. The slight increase in the HHV of raw miscanthus after densification might de due to an experimental error (±0.5 MJ/kg). However, it is interesting to note that the overall volumetric energy density (energy unit per volume) of raw miscanthus increased significantly, from 5.9 to 15.7 GJ/m^3, after densification.

The mass density of the pellets produced from the hydrothermally pretreated miscanthus increased with an increase in the reaction temperature. The pellets produced at 260 °C shows the maximum mass density of 1036 kg/m^3, which is 1.24 times higher than that of the pellet produced from the raw miscanthus. The previous results from the experiments show that the grindability of the biomass increases with an increase in the HTC reaction temperature, thus it makes the material highly friable in nature and easy to compress [17]. The pelletability of the biomass is considerably affected by the small particle size distribution of a feedstock [35]. Hence an increase in the mass density of pellets produced from HTC pretreated miscanthus is directly co-related with the improved grindability of miscanthus (Table 4).

In comparison to the HTC pellets, the mass density of the pellets produced from the torrefied miscanthus was observed substantially lower and similar to that of the raw biomass pellet. Moreover, while measuring the diameter, the pellets produced from the torrefied biomass had slightly larger diameter than that of the raw and HTC pellets. This shows that the internal bonding between the particles of the torrefied biomass was not strong enough to hold tight together as tightly as the raw and HTC pellets.

The chemical composition of a material significantly affects the pelletization process and quality of the pellets [4]. The chemical reaction mechanism that takes place in the HTC process is highly complicated and is only partially understood [27]. The formation of intermediate compounds in the HTC process via condensation and polymerization reactions might have been responsible for the increase in mass and energy density of HTC pellets. Where the formation of such aqueous soluble material is relatively very low in the torrefaction process [34]. The reaction temperature and the type of reaction medium used in the thermochemical process plays an important role in determining the dominancy and rate of reaction mechanism [15].

3.3. Strength and durability of pellets

A durability test is a good tool to predict the strength and quality of the pellets during their supply chain (i.e. from the manufacturing industry to their end use). Durability is defined as the ability of pellets to remain intact while handling and is measured by the amount of dust (fine particles) produced after subjecting

Table 3
Effect of densification on mass density, HHV and energy density.

Process/Pre-treatment	Reaction temperature (°C)	Residence time	Mass density (kg/m^3)	HHV (MJ/kg)	Energy density (GJ/m^3)
Raw	–	–	321.1	18.5	5.9
Pelletization	100	30 s	834.1	18.8	15.7
HTC/Pelletization	190/100	5 min/30 s	886.9	20.2	17.9
HTC/Pelletization	225/100	5 min/30 s	959.4	21.6	20.7
HTC/Pelletization	260/100	5 min/30 s	1035.9	25.9	26.9
Torrefaction/Pelletization	260/100	30 min/30 s	819.6	20.3	16.7

Table 4
Effect of pre-treatment on grindability of biomass.

Material	Particle size distribution (%)			
	>500 µm (%)	250–500 µm (%)	100–250 µm (%)	<100 µm (%)
Raw miscanthus	34.9	46.2	11.1	7.76
HTC-190 °C	17.5	15.7	14.7	52.1
HTC-225 °C	2.8	12.2	18.7	66.5
HTC-260 °C	0.3	1.4	26.2	72.2
Torrefied-260 °C	3.3	42.3	26.6	27.8

the pellets to mechanical or pneumatic agitation [36]. In a similar way, the compression strength of a pellet is the measure of internal bonding strength or the maximum force a pellet can withstand before its rupture during storage. The results for the durability and strength of the raw and pretreated miscanthus pellets are shown in Fig. 7.

The impact resistance durability (IRD) of raw miscanthus pellets was around 92.2% and increased with an increase in HTC reaction temperature (i.e. from 190 to 225 °C). However, the durability of the HTC-260 °C pellet was found to be relatively lower (88.80%) compared to raw and other HTC pellets. The fine particles (<100 µm) of hydrochar are produced in the HTC process at high reaction temperatures. These compacted fine particles of the HTC-260 °C pellets tend to shatter into a powder when dropped onto the metal plate (during IRD test). This explains the low durability of the HTC-260 °C pellets. Further in-depth research on optimization of the pellets shape and pelletization processing conditions may improve the durability of HTC pellets.

The compressive strength of the pellets decreased with an increase in reaction temperature. High percentages of lignin in the material act as a natural binder during pelletization, but at the same time can make the pellets highly brittle. Similar results were obtained in a previous study performed on densification of HTC pretreated loblolly pine wood [20], except for the case of durability. The variation in the results may be due to the different operating conditions such as; the type of feedstock, densification pressure, temperature, and die aspect ratio, that each have strong influences on the physical properties of pellets [4]. On the other hand the pellets produced from torrefied miscanthus were very weak in strength and durability compared to raw and HTC pellets, similar results are also reported in the literature [2,37].

The glass transition temperature (T_g) is the temperature range where a thermosetting polymer changes from a hard, rigid or "glassy" state to a more pliable state. Lignin is the only component of biomass that shows glass transition behavior [20], and it is in the range of 137–157 °C [38]. The moisture content of a feedstock can significantly affect the glass transition temperature of lignin [39]. For the densification of a biomass at the temperatures described above (T_g), a feedstock will show inter-diffusion or formation of a solid bridge between the particles. However, the low densification temperature (100 °C) used in this study might have eliminated the formation of a solid bridge between the particles. The low compression strength of the torrefied pellets may be due to the presence of pores in the hydrochar structure that were observed in earlier previous experiments [17]. The presence of these pores might have reduced the deformation, which indicates the need for a high densification pressure to produce stronger pellets [37].

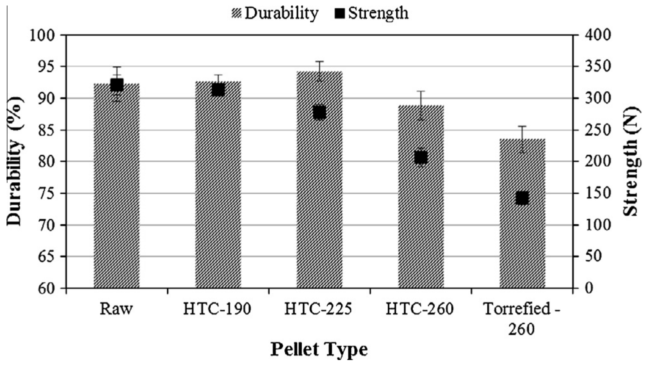

Fig. 7. Effect of pre-treatment type on durability and strength of pellets.

3.4. Hydrophobicity

EMC of a material was used as an indicator of the hydrophobicity. The presence of high moisture content in biomass feedstock/pellets can influence fungal growth and therefore the material will most likely rot with time [40]. Table 5 shows the hydrophobicity of the raw and pre-treated pellets. Both the HTC and torrefaction pre-treatments improved the hydrophobicity of biomass; however, the pellets obtained via HTC were found to be more hydrophobic. The hydrophobicity of the HTC pellets increased with an increase in reaction temperature.

For lignocellulosic biomass, the moisture can be adsorbed in three different ways: (i) free water (present in micro and macro porous capillaries but not to specific sorption sites), (ii) non-freezing bounded water, and (iii) freezing bounded water. Both (ii) and (iii) are hydrogen-bonded to the hydroxyl groups of the cell wall. The non-bounded moisture increases with an increase in relative humidity. Unlike the HTC pretreated miscanthus, due to the volatilization of hemicellulose, the slight porous structures are obtained via dry thermal pre-treatments such as torrefaction and pyrolysis [41]. The presence of pores on the surface of torrefied miscanthus increases the tendency to adsorb moisture content (free water), [42] when compared to HTC pellets.

Table 5
EMC of raw and pretreated pellets before and after immersion.

Pellet	EMC before immersion in water (%)	EMC after immersion in water (%)
Raw miscanthus	6.4	80.9
HTC-190 °C	4.3	66.9
HTC-225 °C	3.3	39.4
HTC-260 °C	2.3	18.6
Torrefied-260 °C	3.8	75.6

Moreover, the chemical composition of biomass has strong influence on the hydrophobic behavior. Among the polymeric composition of biomass, hemicelluloses have the greatest capacity of water adsorption, while lignin shows little tendency for water sorption [40]. Hence, the removal of hemicellulose (or the fractional increase in the lignin content) from a biomass feedstock will improve its hydrophobicity. All these findings support the reason behind the high hydrophobicity of the HTC pellets compared to raw and torrefied pellets.

To determine the strength of the pellets against water resistance, both the raw and pretreated pellets were immersed in water for 2 h. The pellets prepared from the raw miscanthus rapidly separated into fine particles within 15–20 s after immersion in water. The pellets produced via HTC at 190 °C sustained their shape for 5 min and those at 225 °C remained whole for about 30 min. Later these pellets started isolating into discs like structures. The pellets produced from HTC miscanthus at 260 °C remained intact, even after immersion of more than 2 h in water. On the other hand, the pellets produced from the torrefied miscanthus behaved slightly better than raw miscanthus pellets, lasting for about 1–2 min. The hydrophobic behavior of the HTC pellets explains the reason behind the strength against water immersion.

Table 5 shows the moisture content results of samples exposed to room conditions after 2 h of immersion. The results indicate that the pellets produced from the HTC process at 260 °C are highly hydrophobic in nature and therefore can be stored easily without possessing any threat to biological deterioration. Moreover, the transportation of such a feedstock will be less expensive, as there will be less water content to transport along with the biomass.

4. Conclusions

The results show that combining densification with thermal pre-treatments like HTC and torrefaction are a promising method for upgrading biomass, through its conversion to energy dense, homogeneous, friable, and hydrophobic solid fuel. The storage and combustion properties of the HTC pellets were found to be considerably superior compared to torrefied pellets even when with an increased residence time for the torrefaction process (30 min) compared to the HTC process (5 min). The physicochemical properties of the HTC pellets produced at 260 °C were found to be comparable to lignite and are expected to exhibit favorable behavior with respect to combustion, gasification, and other thermal conversion processes. However, it should be noted that at high temperatures, the pressure inside the reactor is also very high. Therefore, in a commercial application of HTC, the high pressure requirement would also increase the process complexity and handling difficulties. Further in-depth research in terms of the techno-economic analysis for the production of HTC and torrefied pellets is required for the comparison of both thermal pre-treatments.

The mass and energy density of the HTC pellets increased with an increase in reaction temperature. In comparison to raw and torrefied pellets, the HTC pellets showed improved hydrophobicity, strong resistance against water immersion, improved grindability, and reduced inorganic elements present in the ash. In addition, the HTC pellets produced at low temperatures (190 and 225 °C) were found to be highly durable. However, the durability reduced with a further increase in reaction temperature. On the other hand, the torrefied pellets showed low mass density and durability even compared to raw miscanthus pellets. Lignin acts as a natural binding agent during the pelletization of biomass; however the high percentage of lignin in pellets makes them highly brittle and weak in strength. The compression strength of the pellets decreased with an increase in the reaction temperature. Therefore, the extension of this work will be focused on the production of spherical shape pellets that may have improved bulk energy density, compression strength, and durability.

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References

[1] Özbay N, Pütün AE, Uzun BB, Pütün E. Biocrude from biomass: pyrolysis of cottonseed cake. Renew Energy 2001;24:615–25.
[2] Wang C, Peng J, Li H, Bi XT, Legros R, Lim C, et al. Oxidative torrefaction of biomass residues and densification of torrefied sawdust to pellets. Bioresour Technol 2013;127:318–25.
[3] Uslu A, Faaij APC, Bergman PCA. Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation. Energy 2008;33:1206–23.
[4] Kaliyan N, Vance Morey R. Factors affecting strength and durability of densified biomass products. Biomass Bioenergy 2009;33:337–59.
[5] Guo W. Self-heating and spontaneous combustion of wood pellets during storage. PhD Dissertation, University of British Columbia, BC, Canada; 2013.
[6] Pimchuai A, Dutta A, Basu P. Torrefaction of agriculture residue to enhance combustible properties†. Energy Fuels 2010;24:4638–45.
[7] Bergman P. Combined torrefaction and pelletisation. The TOP process; 2005.
[8] Bergman P, Boersma A, Zwart R, Kiel J. Torrefaction for biomass co-firing in existing coal-fired power stations. Energy Research Centre of the Netherlands, ECN-C-05-013; 2005.
[9] Shang L, Nielsen N, Stelte W, Dahl J, Ahrenfeldt J, Holm J, et al. Lab and bench-scale pelletization of torrefied wood chips—process optimization and pellet quality. Bioenergy Res 2014;7:87–94.
[10] van der Stelt MJC, Gerhauser H, Kiel JHA, Ptasinski KJ. Biomass upgrading by torrefaction for the production of biofuels: a review. Biomass Bioenergy 2011;35:3748–62.
[11] Kludze H, Deen B, Dutta A. Impact of agronomic treatments on fuel characteristics of herbaceous biomass for combustion. Fuel Process Technol 2013;109:96–102.
[12] Wilén C, Jukola P, Järvinen T, Sipilä K, Verhoeff F, Kiel J. Wood torrefaction-pilot tests and utilisation prospects; 2013.
[13] Mani S, Sokhansanj S, Bi X, Turhollow A. Economics of producing fuel pellets from biomass. Appl Eng Agric 2006;22:421.
[14] Dhungana A, Dutta A, Basu P. Torrefaction of non-lignocellulose biomass waste. Can J Chem Eng 2012;90:186–95.
[15] Libra JA, Ro KS, Kammann C, Funke A, Berge ND, Neubauer Y, et al. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis. Biofuels 2011;2:71–106.
[16] Yan W, Hastings JT, Acharjee TC, Coronella CJ, Vásquez VR. Mass and energy balances of wet torrefaction of lignocellulosic biomass†. Energy Fuels 2010;24:4738–42.
[17] Kambo H, Dutta A. Hydrothermal carbonization (HTC): an innovative process for the conversion of low quality lignocellulosic biomass to hydrochar for replacing coal. In: Proceedings of the 9th annual green energy conference (IGEC-IX), Tianjin, China May 25–8; 2014.
[18] Titirici M-M, White RJ, Falco C, Sevilla M. Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. Energy Environ Sci 2012;5:6796–822.
[19] Reza MT, Uddin MH, Lynam JG, Coronella CJ. Engineered pellets from dry torrefied and HTC biochar blends. Biomass Bioenergy 2014;63:229–38.
[20] Reza MT, Lynam JG, Vasquez VR, Coronella CJ. Pelletization of biochar from hydrothermally carbonized wood. Environ Prog Sustain Energy 2012;31:225–34.
[21] Brosse N, Dufour A, Meng X, Sun Q, Ragauskas A. Miscanthus: a fast-growing crop for biofuels and chemicals production. Biofuels Bioprod Biorefin 2012;6:580–98.
[22] Acharya B, Dutta A. Characterization of torrefied willow for combustion application. J Biobased Mater Bioenergy 2013;7:667–74.
[23] Kaliyan N, Morey RV. Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass. Bioresour Technol 2010;101:1082–90.
[24] Nielsen NPK, Holm JK, Felby C. Effect of fiber orientation on compression and frictional properties of sawdust particles in fuel pellet production. Energy Fuels 2009;23:3211–6.
[25] Khan A, De Jong W, Jansens P, Spliethoff H. Biomass combustion in fluidized bed boilers: potential problems and remedies. Fuel Process Technol 2009;90:21–50.
[26] Reza MT, Lynam JG, Uddin MH, Coronella CJ. Hydrothermal carbonization: fate of inorganics. Biomass Bioenergy 2013;49:86–94.

[27] Funke A, Ziegler F. Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering. Biofuels Bioprod Biorefin 2010;4:160–77.

[28] Bobleter O. Hydrothermal degradation of polymers derived from plants. Prog Polym Sci 1994;19:797–841.

[29] Kambo H. Energy densification of lignocellulosic biomass via hydrothermal carbonization and torrefaction. MASc thesis, University of Guelph, Ontario; 2014.

[30] Demirbaş A. Estimating of structural composition of wood and non-wood biomass samples. Energy Sources 2005;27:761–7.

[31] Liu Z, Quek A, Kent Hoekman S, Balasubramanian R. Production of solid biochar fuel from waste biomass by hydrothermal carbonization. Fuel 2013;103:943–9.

[32] Jenkins BM, Baxter LL, Miles Jr TR, Miles TR. Combustion properties of biomass. Fuel Process Technol 1998;54:17–46.

[33] Huisman W, Venturi P, Molenaar J. Costs of supply chains of Miscanthus giganteus. Ind Crops Prod 1997;6:353–66.

[34] Yan W, Acharjee TC, Coronella CJ, Vásquez VR. Thermal pretreatment of lignocellulosic biomass. Environ Prog Sustain Energy 2009;28:435–40.

[35] Mani S, Tabil LG, Sokhansanj S. Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. Biomass Bioenergy 2006;30:648–54.

[36] Gil MV, Oulego P, Casal MD, Pevida C, Pis JJ, Rubiera F. Mechanical durability and combustion characteristics of pellets from biomass blends. Bioresour Technol 2010;101:8859–67.

[37] Li H, Liu X, Legros R, Bi XT, Jim Lim C, Sokhansanj S. Pelletization of torrefied sawdust and properties of torrefied pellets. Appl Energy 2012;93:680–5.

[38] Grāvitis J, Ābolinš J, Tupčiauskas R, Vēveris A. Lignin from steam-exploded wood as binder in wood composites. J Environ Eng Landscape Manage 2010;18:75–84.

[39] Stelte W, Clemons C, Holm JK, Ahrenfeldt J, Henriksen UB, Sanadi AR. Thermal transitions of the amorphous polymers in wheat straw. Ind Crops Prod 2011;34:1053–6.

[40] Acharjee TC, Coronella CJ, Vasquez VR. Effect of thermal pretreatment on equilibrium moisture content of lignocellulosic biomass. Bioresour Technol 2011;102:4849–54.

[41] Fuertes A, Arbestain MC, Sevilla M, Maciá-Agulló J, Fiol S, López R, et al. Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonisation of corn stover. Soil Res 2010;48:618–26.

[42] Stelte W, Clemons C, Holm JK, Sanadi AR, Ahrenfeldt J, Shang L, et al. Pelletizing properties of torrefied spruce. Biomass Bioenergy 2011;35:4690–8.